Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Selective Growth of MFU-4*l* Single Crystals on Microstructured Plasma Polymer Coatings

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Details on experiments:

The FEMTO plasma system (Diener features two power generators, the first working at a frequency of 13.56 MHz while the other one is operated at 40 kHz; both offer pulsed and continuous modes at a maximum power output of 300 W. The pressure of the volatile monomers introduced into the reaction chamber ranges from 0.1 to 0.8 mbar. The volume of the reaction chamber is approximately 6 dm^3.
Ahead of deposition processes the glass substrates were etched by oxygen plasma to remove any organic residues from the glass surface. The conditions for the etching and deposition steps are shown in Table S1.

Table S1: Conditions used for deposition and etching processes.

	O_2	ppHMDSO	ppPA	ppH
Power [W]	300	150	150	150
Frequency	13.56 MHz	40 kHz	40 kHz	40 kHz
Mode	continuous	pulsed	pulsed	pulsed
Duration [min]	30	1	90	2
Pressure [mbar]	0.30	0.50	0.55	0.60

UV lithography was performed at ambient conditions for 90 min, employing a custom-made UV-lithography system. The system consists of a Hamamatsu LC8 unit (Japan) containing a 250 nm 200 W mercury-xenon lamp.

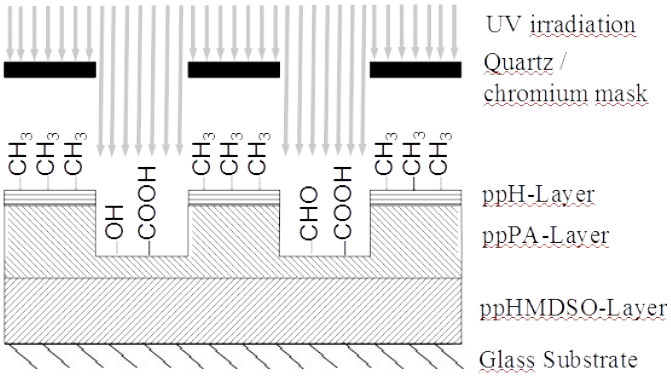

Fig. S1: Schematic structure of the patterned plasma coating.

X-ray photoelectron spectroscopy (XPS):

The XPS device (Omicron) features a monochromatic Mg anode (XM 1000 Mk II, 1486.7 eV) and a hemispherical analyzer (EA 125). For XPS measurements silicon wafer substrates were used instead of glass substrates, because the substrate has to be conductive. The plasma etching and all deposition steps were carried out identically as with glass substrates. Also, for XPS measurements the UV irradiation was performed on the whole coating surface without employing a mask.

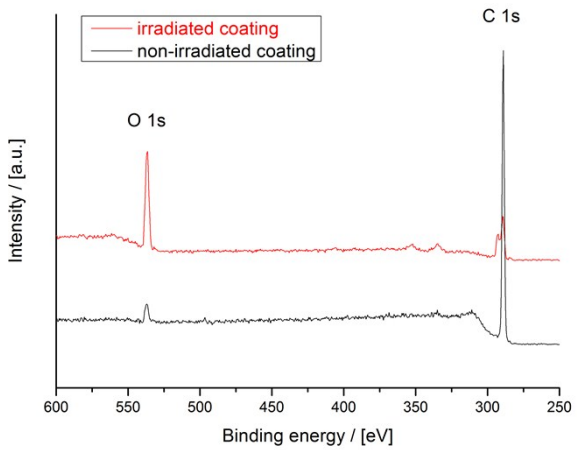

Fig. S2: XPS spectra of non-irradiated and irradiated plasma polymer coatings.

Auger spectroscopy, Auger mapping:

Auger spectroscopy and Auger mapping scans were performed employing a NANO-SAM (Omicron). Instead of glass silicon was chosen as substrate material and etching, deposition steps as well as UV lithography were carried out identically as with glass substrates. Additionally the prepared samples were immersed into a 0.5 M solution of $ZnCl_2$ for 30 min at 150 °C. Fig. S2 represents two representative Auger spectra of hydrophobic or hydrophilic areas after immersion in $ZnCl_2$ solution. The binding energy of the zinc signal is shifted by approx. 4 eV due to charging of the sample surface during the measurement.

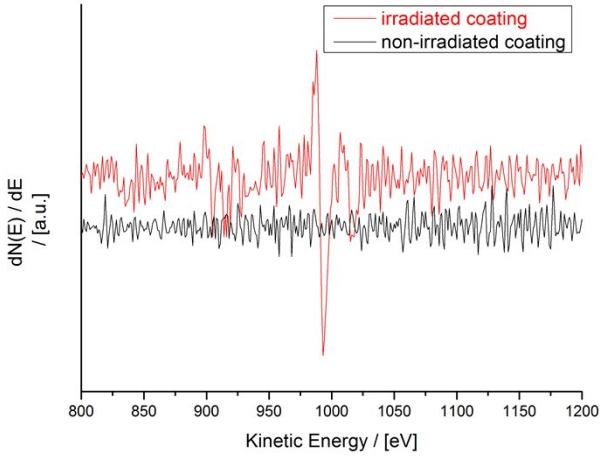

Fig. S3: First-derivative Auger spectra of non-irradiated and irradiated plasma polymer coatings after immersion in $ZnCl_2$ solution. No zinc signal is detected for the non-irradiated parts of the sample (black line), in contrast to the distinct zinc 2p line observed at 993 eV (red line), accounting for the irradiated and UV etched film surface.

For the scanning Auger mapping the Zn 2p peak intensity at 993 eV was used in combination with the intensity at 1025 eV serving as background signal. The background corrected map was generated by the formula $I = \frac{p - b}{p + b}$, where *I* is the corrected intensity, *p* represents the zinc peak intensity and *b* the background intensity.

Scanning electron microscopy (SEM):

SEM micrographs were carried out with a XL 30 ESEM FEG (FEI), in High Vacuum Mode. The samples were sputter-coated with gold for 30 s before measurement.

Atomic force microscopy (AFM) measurements:

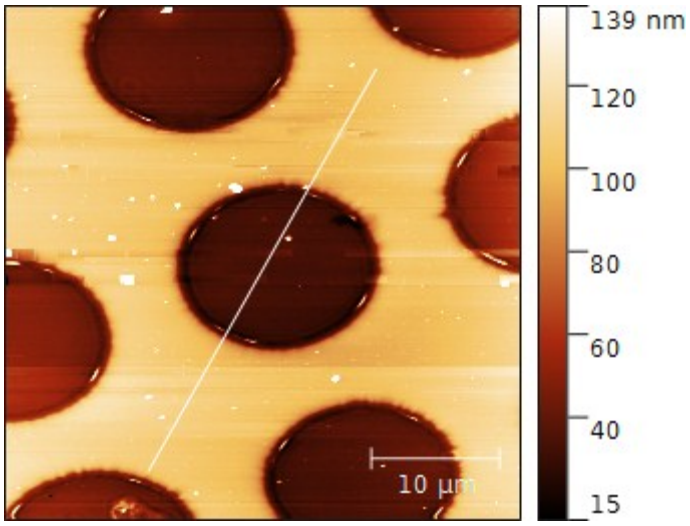

Fig. S4: False colour atomic force microscopy image of a glass substrate with plasma coating after 90 min UV irradiation through a quartz / chromium mask. The black circles correspond to the irradiated areas. The white line represents the topography shown in Figure S2.

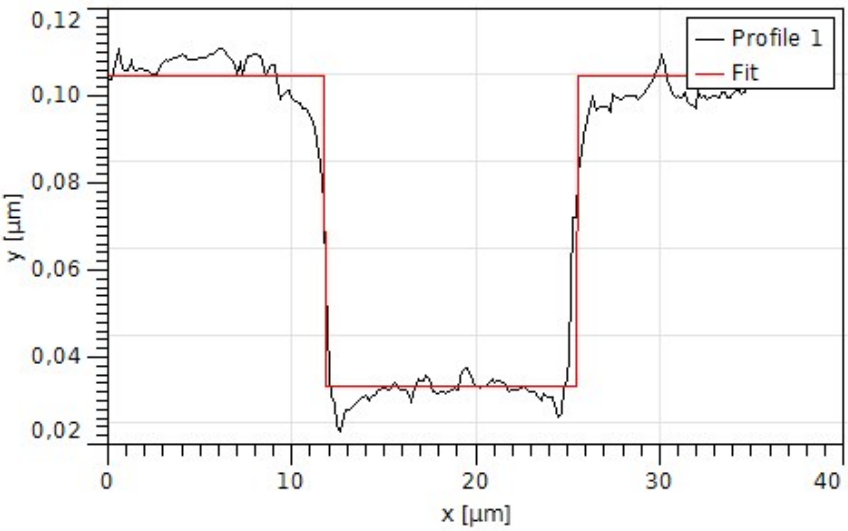

Fig. S5: The topography scan (black line) and step height fit (red line) of the AFM image shown above. The step height is 71.1 ± 4 nm.

MFU-4*l* synthesis

In a closed reaction vessel 12 mg (0.044 mmol) of the linker H_2-BTDD (= bis (1*H*-1,2,3-triazolo[4,5-b],-[4',5'-i])dibenzo[1,4]dioxin) were dissolved in 10 mL DMF at 150 °C for 60 min. After the organic linker had completely dissolved, a solution of 122 mg (0.900 mmol) $ZnCl_2$ in 1.8 mL DMF was added.

A glass substrate coated with a micro-patterned plasma polymer film was directly placed in the reaction vessel on a small PTFE ring, with the coating facing downward. The closed reaction vessel was heated at 150 °C for 90 min. After cooling the reaction medium down to room temperature the glass substrate was removed from the vessel and rinsed twice with ethanol (p.a.).

Optical microscopy:

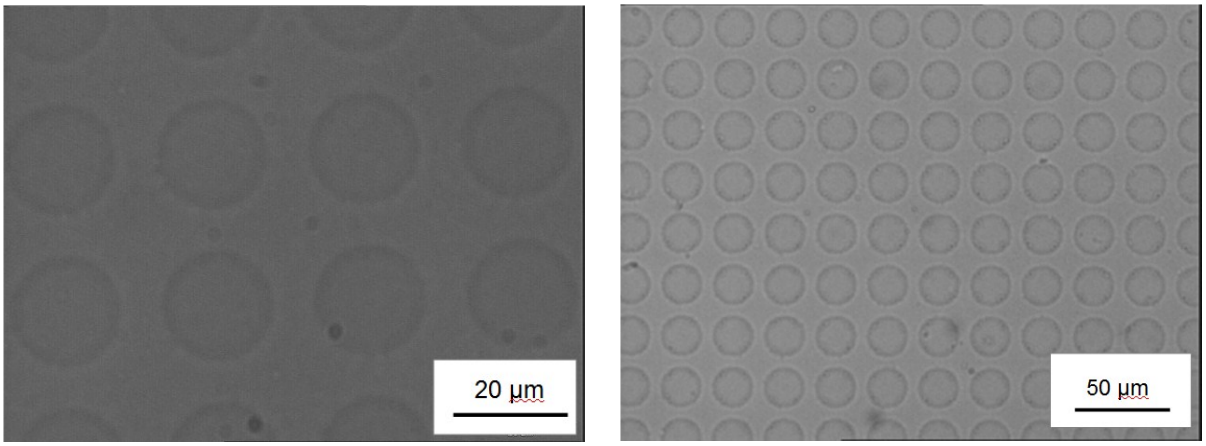

Fig. S6: Differential interference contrast micrographs of a UV etched plasma coating after immersion in 0.5 M $ZnCl_2$ solution at 150 °C for 90 min. The coatings show no sign of damage or delamination.

X-ray powder diffraction:

XRD measurements were carried out with a Seifert X-ray diffraction system 3003 PTS HR (40 kV, 40 mA, Cu Kα (λ = 1.54178 Å) equipped with a 4 circle goniometer set up. The sample consisting of the glass substrate, the UV etched plasma coating and the MOF crystals were mounted without further preparation on the goniometer sample stage. 2Theta and Omega scans were performed with a step size of 0.02° and a step time of 1 s.

Table S2 Crystal orientation and corresponding integrated reflex intensities of the simulated XRD pattern and the measured XRD pattern and the resulting factor and relative frequency of the crystal orientation.

hkl	simulated integral	rel. frequency	measured integral	rel. frequency
2 0 0	1500	33.3 %	370000	90 %
2 2 0	250	33.3 %	3900	4 %
3 1 1	50	33.3 %	760	6 %